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MEASUREMENT OF NITROGEN OXIDE (NO_x) EMISSIONS IN FUEL-COMBUSTION EQUIPMENT AND ANALYSIS OF THEIR IMPACT ON CITY AIR CONDITION

The object of the research is to ensure environmental safety and maximum efficiency of fuel burning equipment. Energy facilities (thermal power plant, boiler houses) are among the biggest air polluters in the city. Nitrogen oxides (NO, NO₂, NO_x) occupy a significant place among the toxic gases contained in the flue gases of fuel-burning equipment. These substances have a negative impact on the ecological state of the city and are regulated by the Order of the Ministry of Natural Resources of Ukraine dated 27.06.2006 No. 309 on the approval of standards for maximum permissible emissions of pollutants from stationary sources. The principles of measurement unity are considered, including the presentation of measurement results in standard units (ppm, mg/m³). Conversion from volume concentration (ppm) to mass (mg/m³) is given. Measurements of the concentration of nitrogen oxides were carried out. In the course of research, instrumental measuring tools were used, which made it possible to obtain the values of nitrogen dioxide concentrations in gas boiler flue emissions. In particular, the average maximum concentrations of the main pollutants exceed 62.58 mg/m³. Analyzing the concentration of flue gases allows to determine the concentration of pollutants and to adjust the optimal operation of the equipment as much as possible, achieving a reduction in emissions and compliance with the approved emission standards. Obtained data on background concentrations of nitrogen dioxide in the city of Kyiv, amounting to 1.33 MPC. Using the data of instrumental measurements with the method of calculating concentrations of harmful substances in the atmospheric air and background concentrations, a map of emission dispersion was created. Fields of surface concentrations were plotted on the scattering map, which makes it possible to compare the obtained values with the hygienic standards of atmospheric air. By combining instrumental measurement methods and calculation methods, the volume of emissions was determined and the impact on atmospheric air pollution of the city was assessed.

Keywords: pollutant emissions, nitrogen oxides, gas analyzer, emission dispersion map, hygienic standards of atmospheric air.

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1. Introduction

The rapid development of cities, the concentration of a large number of people, vehicles, industrial and energy facilities in megacities and cities leads to intensive pollution of the atmosphere with harmful emissions. A special place among these sources of emissions is occupied by energy facilities: thermal power plants and power plants, boiler houses, firing furnaces, metallurgical plants, generators, and other fuel-burning equipment. These energy facilities, on the one hand, are the backbone of the country's economy, and on the other, they are one of the main pollutants of the atmosphere, especially that part of it that runs on solid fuel: coal, peat, wood, pellets [1, 2]. These organic fuels, which are used to obtain electrical or thermal energy, usually have nitrogen in their composition along with hy-

drogen and carbon. As a result of their combustion, various combustion products are formed, such as carbon monoxide CO, carbon dioxide CO₂, water vapor H₂O, nitrogen oxides (NO+NO₂=NO_x).

One of the main goals of environmental protection is the elimination of harmful flue gas emissions or their maximum reduction [3]. One of the most toxic components in the emissions of energy facilities are nitrogen oxides, which contribute to the occurrence of acid rain, smog, cause suffocation, and decay of lung tissue in people and animals, especially for thermal power plants operating on coal [4]. Emissions of nitrogen oxides are regulated in the atmospheric air and in technological processes related to combustion: heating plants, boilers operating on sunflower husks, plants for burning and agglomeration of metal ore, plants for burning ferroalloys, glass production, etc. [5].

The key to the optimal operation of fuel-burning equipment is to establish the volume of air supplied for combustion and measure the concentration of nitrogen oxides and oxygen with gas analyzers, flowmeters, and gas and dust flow speed and temperature meters in smoke pipes.

However, the analysis of emissions of nitrogen oxides by a fuel-burning facility and their distribution, especially in the conditions of urban agglomerations of various buildings, is not carried out in full [6]. Also, the use of modern measuring tools is performed without analyzing the optimal place of sampling, features of concentration calculation and taking into account the uncertainty of gas analyzer measurements [7].

The aim of research is to determine the peculiarities of measuring the concentration of nitrogen oxides in the emissions of fuel-burning equipment during the technological process of using a typical boiler at a natural boiler house with a capacity of up to 10 mW.

To achieve the aim, the following objectives must be solved:

1. Justify the method of reducing the concentration of nitrogen oxide to nitrogen dioxide and converting it to the standard oxygen content.
2. Based on the instrumental method of measurement and calculation methods, determine the volume and concentration of emissions of nitrogen oxides.
3. Create a mathematical model of emissions dispersion.
4. Establish the factors affecting the level of air pollution in the city by nitrogen dioxin.

2. Materials and Methods

When conducting an instrumental analysis of the gaseous composition of combustion products, gas analyzers based on the selective identification of individual components are used. The means of measurement are based on the determined volume concentration. Such a representation of concentration was formed under the influence of tradition, since for a long time in analytical chemistry the volume-manometric method of gas analysis prevailed, and in engineering it was customary to keep records of gas by volume. Volume concentration is the ratio of the volume of a specific substance to the volume of the entire gas sample and can be measured as a percentage of volume (% vol) or ppm. This, in turn, introduces certain discrepancies between the measurement results and state regulations, which set the maximum permissible emissions from emission sources in mg/m³. To compare the measured values (ppm) with the standard ones (mg/m³), a conversion is used. In the case of nitrogen oxide NO and nitrogen dioxide NO₂, the obtained values in units (ppm) are multiplied by a factor of 2.05. In this case, the obtained concentration is the sum of oxide and nitrogen dioxide and is denoted by NO_x:

$$C_{\text{NO}_x} = 2.05 \cdot (M_{\text{NO}} + M_{\text{NO}_2}), \quad (1)$$

where C_{NO_x} – mass concentration of nitrogen oxides, in terms of nitrogen dioxide, mg/m³; M_{NO} – volume concentration of nitrogen oxide, ppm; M_{NO_2} – volume concentration of nitrogen dioxide, ppm.

When recalculating measurement results from volume units to mass, values are obtained that do not depend on temperature and pressure and are reduced to normal conditions (pressure 760 mm Hg and temperature 0 °C).

For fuel-burning equipment, the results of mass concentration measurements are converted to dry gas and stan-

dard oxygen content. For this, additional measurements of the content of oxygen O₂ and moisture H₂O in the waste gases of combustion products are performed. Depending on the method of instrumental measurement, determination of concentrations of nitrogen dioxide NO_x is performed in wet or dry waste gases. Obtaining the mass concentration in dry waste gases is achieved by using gas analyzers equipped with a sample preparation system (drying and condensation or a condensate collector). In the case of using the sample preparation system, recalculation of mass concentration to dry gas is not carried out. Bringing the mass concentration to the standard oxygen content in dry waste gases is carried out according to the formula:

$$C_{n.c.(O_2)} = C_{n.c.} \cdot (21 - O_{2ST}) / (21 - O_{2M}), \quad (2)$$

where $C_{n.c.(O_2)}$ – mass concentration of the pollutant in dry waste gases, mg/m³; $C_{n.c.}$ – mass concentration of pollutant in dry waste gases, mg/m³; O_{2ST} – standard oxygen content in dry waste gases, %; O_{2M} – measured oxygen content in dry waste gases, %.

Today, there are three most common methods of gas analysis: electrochemical, infrared and chemiluminescent. The electrochemical method is used for one-time inspection control of nitrogen oxides, the infrared method allows measuring only NO, the chemiluminescent method provides both control of NO and NO₂ separately, and determination of their total NO_x. For inspection, periodic control of nitrogen oxides, the electrochemical method is most often used [8].

An autonomous rooftop boiler room of a multi-story residential building was taken for the study of emissions of pollutants from boilers operating on natural gas. The composition of this boiler house includes five gas boilers «Viessmann Vitoplex 300 TX3» (Germany), capacity 1750 kW each. The roof boiler room is used for heat supply of the heating, ventilation and hot water supply system for the consumers of the residential building. The boilers work alternately, but the mode of operation also provides for their simultaneous use depending on the needs. Emissions of polluting substances are formed as a result of the processes of burning the specified fuel in boiler units.

Table 1 shows technical data on boiler units, time and mode of operation.

Table 1

Technological equipment

Name	Quantity	Productivity	Balance of time per year, h/year
Boiler «Viessmann Vitoplex 300 TX3»	5	1750 kW	2160

The input data are the results of instrumental measurements of environmental parameters of boiler units, which were carried out with the help of measuring devices: gas analyzers, speed, temperature and volume flow meters of gas and dust flows in accordance with the requirements of DSTU 8725:2017 and DSTU 8812:2018 [9, 10]. Quantitative values of nitrogen dioxide concentrations determined for each boiler are given in Table 2. Instrumental studies were carried out according to the approved methods of measuring polluting quantities and other parameters (temperature, pressure, consumption) of gas and dust flow in emissions from boiler units when using gas.

Concentrations of pollutant sources and gas and dust flow parameters of boiler units

Table 2

The source of pollutant formation	Volumetric gas consumption, m ³ /s	Temperature, °C	Pollutant		The value of the concentration of pollutants, mg/m ³ (adjusted to n.c. and st. O ₂)	
			Code	Name	Max	Min
Boiler No. 1	0.677	142	301	Nitrogen dioxide	49.07	45.37
Boiler No. 2	0.676	141	301	Nitrogen dioxide	49.7	46.15
Boiler No. 3	0.679	145	301	Nitrogen dioxide	46.22	42.73
Boiler No. 4	0.676	133	301	Nitrogen dioxide	56.02	50.6
Boiler No. 5	0.674	142	301	Nitrogen dioxide	62.58	58.9

The portable gas analyzer «OKSI 5M» (Ukraine) was used for the measurement, which is designed for environmental and thermotechnical measurements of the volume concentration of oxygen O₂, CO, NO, NO₂ and SO₂ in flue gases and the temperature of flue gases. Gas analyzers of this series are used in the maintenance of power plants, environmental control, repair and adjustment of fuel-burning equipment.

3. Results and Discussion

The roof boiler room is equipped with «Viessmann Vitoplex 300 TX3» boilers – 5 units with a capacity of 1750 kW each, operating on natural gas. The total consumption of natural gas is 800,000 m³/year. Each boiler is equipped with a separate smoke pipe with parameters $H=86.0$ m (the roof boiler room is located on the roof at a height of 75 m), $D=0.5$ m. Operating time – 2160 h/year. Pollutants: nitrogen oxides (nitrogen oxide and dioxide) in terms of nitrogen dioxide, carbon monoxide, methane, carbon dioxide, nitrogen (1) oxide [N₂O], mercury and its compounds (in terms of mercury).

The calculation of emissions of harmful substances emitted into the atmosphere during the combustion of organic fuel is carried out according to [11].

The gross emission of the j -th pollutant E_j entering the atmosphere with the flue gases of the power plant during the time period P is determined by the formula:

$$E_j = \sum_i E_{ji} = 10^{-6} \sum_i k_{ji} B_i (Q^f)_i, \quad (3)$$

where E_{ji} – the gross emission of the j -th pollutant during the burning of the i -th fuel during the time period P , t; k_{ji} – emission index of the j -th pollutant for the i -th fuel, g/GJ; B_i – consumption of i -th fuel during the time period P , t; $(Q^f)_i$ – the lower working heat of combustion of the i -th fuel, MJ/kg.

Characteristics of natural gas used at the enterprise in accordance with the gas quality protocol (Table 3).

The specific emission indicator is determined on the basis of measurements of the concentrations of pollutants (adjusted to the standard oxygen content of O₂=3 %), given in Table 4.

The determination of the gross pollutant emission according to formula (3) is given in Table 5.

Calculations were made according to the methodology for «Viessmann Vitoplex 300 TX3» boilers (5 units). Summarized estimated data on the level of emissions of nitrogen dioxide NO_x from the boilers of the roof gas boiler house are given in Table 6. These values were used to assess the impact on the state of air pollution of the city by nitrogen dioxide NO_x.

Characteristics of gas

Table 3

Sampling location	CH ₄ , mol. %	C ₂ H ₆ , mol. %	C ₃ H ₈ , mol. %	C ₄ H ₁₀ , mol. %	C ₅ H ₁₂ , mol. %	C ₆ H ₁₄ , mol. %	CO ₂ , mol. %	N ₂ , mol. %	Q _f , MJ/m ³	ρ _n , kg/m ³
TPP-6	89.4032	5.0112	1.1106	0.3157	0.1013	0.1053	2.3148	1.6310	38.1933	0.6284

Specific emission indicators

Table 4

Boiler No.	Measured mass concentration, mg/m ³	Emission coefficient of nitrogen oxides, g/GJ
1	$C_{O_2=3\%}^{NO_x} = 49.07$	$\frac{49.07 \cdot 12.666}{45.728} \cdot 1 \cdot \left(1 - \frac{2}{100}\right) = 13.32$
2	$C_{O_2=3\%}^{NO_x} = 49.70$	$\frac{49.70 \cdot 12.666}{45.728} \cdot 1 \cdot \left(1 - \frac{2}{100}\right) = 13.49$
3	$C_{O_2=3\%}^{NO_x} = 46.22$	$\frac{46.22 \cdot 12.666}{45.728} \cdot 1 \cdot \left(1 - \frac{2}{100}\right) = 12.55$
4	$C_{O_2=3\%}^{NO_x} = 56.02$	$\frac{56.02 \cdot 12.666}{45.728} \cdot 1 \cdot \left(1 - \frac{2}{100}\right) = 15.21$
5	$C_{O_2=3\%}^{NO_x} = 62.58$	$\frac{62.58 \cdot 12.666}{45.728} \cdot 1 \cdot \left(1 - \frac{2}{100}\right) = 16.99$

Gross pollutant emission

Table 5

Boiler No.	Gross emission of nitrogen oxides, t/y
1	$E_{NO_2} = 10^{-6} \cdot 13.32 \cdot 45.728 \cdot 120.6343 \approx 0.073478$
2	$E_{NO_2} = 10^{-6} \cdot 13.49 \cdot 45.728 \cdot 120.6343 \approx 0.074416$
3	$E_{NO_2} = 10^{-6} \cdot 12.55 \cdot 45.728 \cdot 120.6343 \approx 0.06923$
4	$E_{NO_2} = 10^{-6} \cdot 15.21 \cdot 45.728 \cdot 120.6343 \approx 0.083904$
5	$E_{NO_2} = 10^{-6} \cdot 16.99 \cdot 45.728 \cdot 120.6343 \approx 0.093723$

Estimated emission power

Table 6

Boiler No.	Pollutant	mg/m ³	g/s	t/year
1	Nitrogen dioxide	49.07	0.012984	0.073478
2	Nitrogen dioxide	49.7	0.013156	0.074416
3	Nitrogen dioxide	46.22	0.012235	0.06923
4	Nitrogen dioxide	56.02	0.014821	0.083904
5	Nitrogen dioxide	62.58	0.016563	0.093723

In order to assess the impact of emission sources on the state of atmospheric air pollution, data on background concentrations of nitrogen dioxide were obtained in the city of Kyiv, post No. 6. The data were provided by the Borys Sreznevsky Central Geophysical Observatory (CGO). The value of the background concentration of nitrogen dioxide is given in Table 7.

Using the «EOL+» software complex, which implements the «Methodology for calculating concentrations in atmospheric air of harmful substances contained in the emissions of enterprises. OND-86», which regulates the calculation of dispersion and determination of surface concentrations. The resulting fields of concentrations make it possible to estimate the level of influence on atmospheric air pollution. The calculation was carried out at background concentrations.

Fig. 1 shows the dispersion zones of pollutants, the values are presented in fractions of MPC (maximum permissible concentration) for a better comparison with normative values of MPC.

The result of calculating the dispersion of nitrogen dioxide from boiler emissions in the surface layer of the atmosphere showed the maximum concentration values at a distance of 263 m from the emission source, without taking into account the background, is 0.01 MPC. At the same time, the surface concentration obtained in the calculation of scattering taking into account the background is 1.34 MPC.

Background concentrations of nitrogen dioxide in the city of Kyiv post No. 6

Table 7

Coordinates		Pollutant	MPC _{m.y.} , mg/m ³	Background concentration, mg/m ³				
				Wind speed, m/s				
width	length			0–2	More than 3			
				Any	North	East	South	West
50°26'52.14"	30°29'27.09"	Nitrogen dioxide	0.2	0.26626	0.31009	0.31009	0.31009	0.31009

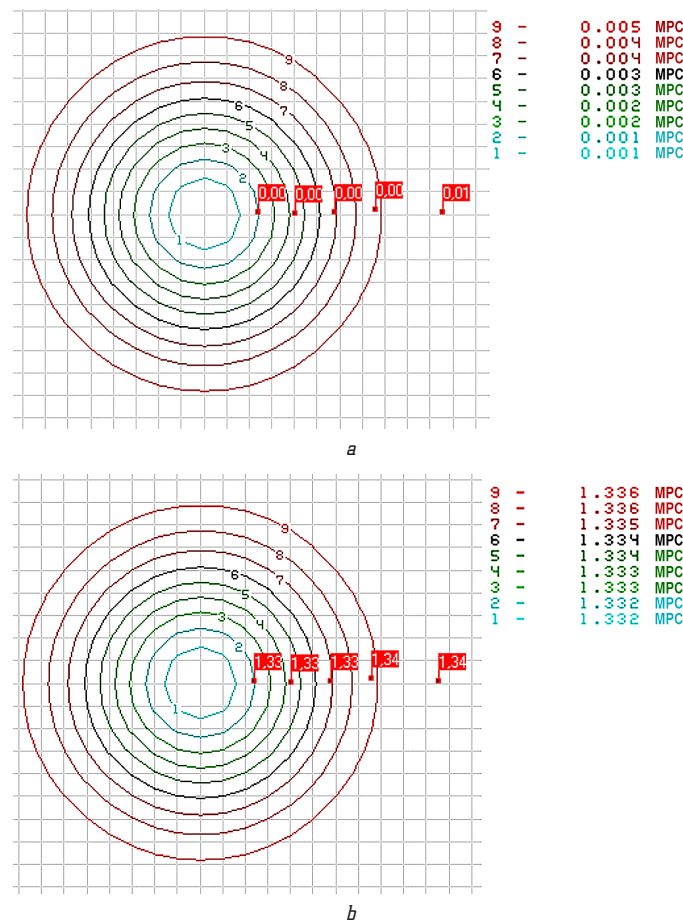


Fig. 1. Nitrogen dioxide diffusion zones:

a – without taking into account the background concentration; *b* – taking into account the background concentration

Therefore, the cause of the high level of nitrogen dioxide in the air of the city, along with emissions from boiler plants, is emissions from other sources. In particular, motor vehicles can be singled out among these sources. So, for example, in London in the mid-90s, before the implementation of measures to reduce the city's air pollution, 74 % of NO_x emissions was the result of automobile traffic [12].

It is advisable to conduct a study of the impact of emissions from motor vehicles for a comprehensive assessment of the impact of anthropogenic emission sources on air pollution in the city.

The obtained results can be practically applied when issuing permit documents: a permit for emissions of stationary sources (Article 10 of the Law «On Protection of Atmospheric Air»), environmental impact assessment (Law «On Assessment of Impact on the Environment») in the part of real evidentiary impact on the environment. And also when developing measures to reduce air pollution in the city.

The limitation is that the results of these studies should only be used to estimate emissions from residential buildings or enterprises with their own gas boiler room.

In the conditions of martial law, many enterprises do not fulfill the requirements of environmental protection legislation, and the use of diesel and gasoline generators has also increased, which in turn increases the levels of emissions and the general background of pollutants in the atmospheric air of the city.

4. Conclusions

The reduction of the concentration of nitrogen oxide to nitrogen dioxide and the conversion to the standard oxygen content are substantiated, which ensures the unity of measurement of emissions from fuel-using equipment.

In the course of the study, the average concentrations of nitrogen dioxide from five boiler units with a capacity of 1750 kW each, operating on natural gas and not exceeding 62.58 mg/m³, were determined. On the basis of the measurements of concentrations and calculation methods, the volume of emissions for each boiler was determined.

Using a mathematical model of dispersion, a map of the dispersion of nitrogen dioxide produced during the combustion of natural gas in boiler units and their simultaneous operation was created. The scattering calculation was performed with and without taking into account the background concentration of nitrogen dioxide. According to their results, the concentration of nitrogen dioxide without the background does not exceed the value of 0.01 MPC, while taking into account the background it is 1.34 MPC.

The research results showed that the use of gas boilers with a total capacity of up to 8.75 mW does not lead to excessive air pollution. Concentrations of nitrogen dioxide do not exceed the value of 1 MPC and are 0.01 MPC. It should also be noted that the dispersion zone is affected by the height of the chimney and the dangerous wind speed. The reason for exceeding the MPC levels for nitrogen dioxide in the city of Kyiv may be motor

vehicles, which account for 50 % of the total NO_x emissions, and this share is even higher in cities.

Conflict of interest

The author declares that he has no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

The manuscript has no associated data.

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